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(54) TITLE OF THE INVENTION

Manufacturing Method for a Metal Plate Laminated with Film Having an Ink Layer

(57) ABSTRACT

PURPOSE

To obtain a plastic film-laminated metal plate with an ink layer which has excellent adhesion between a transparent plastic film, ink, and metal plate, excellent processing properties when used to make cans, and which has excellent surface finish and retort resistance properties, and the like.

CONSTITUTION

Laminate a metal plate with an electron beam-hardening adhesive layer having between 0.5 and 250 weight parts of a stress-relaxing agent in 100 weight parts of a resin composition formulated with between 2 and 200 weight parts of polyester oligomer with polymeric unsaturated double bonds in 100 weight parts of polyester resin, an electron beam-hardening ink layer containing a colorant and a resin composition formulated with between 2 and 200 weight parts of oligomer polyester with polymeric unsaturated double bonds in 100 weight parts of polyester resin, and a polyester film, and said adhesive layer and said ink layer are hardened by irradiating with an electron beam.

[Claims]

What Is Claimed Is:

Claim 1

A manufacturing method for a plastic film-laminated metal plate with an ink layer in which an adhesive layer, ink layer, and transparent plastic film are successively overlaid on a metal plate, wherein:

the adhesive layer is consisting of an electron beam-hardening adhesive containing between 0.5 and 250 weight parts of stress-relaxing agent and 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of a polyester oligomer with an arithmetic mean molecular weight of between 300 and 5000 having between 0.3 and 5.0 mole/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000;

the ink layer consisting of an electron beam-hardening ink containing a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyester oligomer with an arithmetic mean molecular weight between 300 and 5000 having between 0.3 and 5.0 mol/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000; and the electron beam-hardening adhesive and the beam-hardening ink, and the like, are hardened by irradiating with an electron beam through the laminated transparent plastic film.

Claim 2

The manufacturing method according to Claim 1, wherein the transparent plastic film is a polyester film.

Claim 3

The manufacturing method according to Claim 1 or Claim 2, wherein the metal plate which is laminated with a film having an ink layer is a film-laminated metal plate for making cans.

DETAILED DESCRIPTION OF THE INVENTION

[0001] INDUSTRIAL FIELD OF APPLICATION

Present invention relates to a metal plate which is laminated with an electron beam-hardening adhesive, an electron beam-hardening ink, and a transparent plastic film.

[0002] BACKGROUND TECHNOLOGY AND PROBLEMS THEREOF TO BE RESOLVED

Conventionally, metal plate which has been laminated with a transparent plastic film with an ink layer which is used for cans for beverages and cans for food (hereinafter referred to as "film-laminated metal plate") normally consist of a metal plate overlaid with a transparent plastic film such as a polyester film with an ink layer using an adhesive (for instance, refer to Japanese Unexamined Patent Application H3-87249, and the like).

[0003] The manufacturing method for conventional film-laminated metal plate for instance consists of (1) a step of printing ink on a polyester film (hereinafter referred to as "PET film") which is the transparent plastic film, drying, applying an adhesive thereon, and then drying until tack-free (normally at approximately 50°C to 150°C for several seconds); or (2) a step of hardening by heating (normally at approximately 180°C for 0.5 seconds) and compressing a PET film onto which ink and adhesive have been applied, onto a metal plate.

[0004] The aforementioned conventional manufacturing method has the following problems.

1. In order to meet conditions for manufacturing film-laminated metal plate using a high-speed production line necessary for large volume production, the after bake oven must be lengthened and this equipment is large so the equipment expense will increase and more plant space will be required.

2. With a conventional manufacturing method, if the lamination speed exceeds 150 m/min, or if the lamination temperature is below 180°C, areas without sufficient adhesion (insufficient hardening) will appear, and there will be variations in appearance.

3. A can for beverages or a can for food manufactured from film-laminated metal plate obtained by a conventional method has poor processing properties (necking process, flanging process, beading process, and the like) and because of the heat from baking (maximum temperature between 230°C and 240°C for 90 seconds or between 240°C and 280°C for between 7 and 20 seconds) the side seam paint and the heat of welding at the can body seam line in the area of the weld may have whitening or blistering occur after retort processing, a pattern similar to water spots may appear on the surface of the PET film, and surface finish will be poor because of reduced gloss, and the like.

[0005] In order to resolve the aforementioned problems, the present inventors have previously proposed in Japanese Unexamined Patent Application H6-192637 a method for obtaining a film-laminated metal plate using an electron beam hardened adhesive as the adhesive, and after overlaying a polyester film onto a metal plate using electron beam-hardening adhesive, an electron beam is irradiated through the polyester film in order to harden the adhesive.

[0006] These problems could be resolved using the method according to this proposal, but normally a lacquer-type gravure ink is used as the ink, so there were problems with poor adhesion in the processing regions, and whitening and blistering readily occurring in the forming regions because of the retort process.

[0007] With the foregoing in view, an object of the present invention is to provide a film-laminated metal plate with excellent adhesion between the transparent plastic film, ink, and metal plate, and having superior performance in such areas as processability when used to make cans, ability to withstand retorting not only in flat regions but also in formed regions, and superior surface finish when compared to conventional products, without the need for large equipment and space by laminating at high speed and low temperature using electron beam hardening of the ink and adhesive.

[0008] MEANS FOR RESOLVING PROBLEMS
As a result of diligent research to resolve the aforementioned problems, the present inventors have discovered that the aforementioned objectives can be achieved by using electron beam-hardening materials of a specific composition for the adhesive and ink of the film-laminated metal plate, and then hardening by electron beam, and have thus achieved the present invention.

[0009] In other words, the present invention provides:
1. A manufacturing method for a plastic film-laminated metal plate with an ink layer wherein an adhesive layer, ink layer, and transparent plastic film are successively overlaid on a metal plate, wherein:
the adhesive layer is consisting of an electron beam-hardening adhesive containing between 0.5 and 250 weight parts of stress-relaxing agent and 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of a polyester oligomer with an arithmetic mean molecular weight of between 300 and 5000 having between 0.3 and 5.0 mole/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000;
the ink layer is consisting of an electron beam-hardening ink containing a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyester oligomer with an arithmetic mean molecular weight between 300 and 5000 having between 0.3 and 5.0 mol/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000; and the electron beam-hardening adhesive, and the like, and beam-hardening ink are hardened by irradiating with an elec-

tron beam through the laminated transparent plastic film.

[0010] Furthermore, the present invention 2 provides the manufacturing method according to item 1 above, wherein the transparent plastic film is a polyester film.

[0011] Moreover, the present invention 3 also provides the manufacturing method according to item 1 or 2 above, wherein the metal plate which is laminated with a film having an ink layer is a film-laminated metal plate for making cans.

[0012] FUNCTION

The present invention will be described below in detail. The electron beam-hardening adhesive of the present invention is comprising between 0.5 and 250 weight parts of a stress-relaxing agent in 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of polyethylene oligomer (hereinafter referred to as "oligomer") with an arithmetic mean molecular weight between 300 and 5000 and having between 0.3 to 5.0 mol/kg molecules with polymeric unsaturated double bonds in 100 weight parts of polyester resin.

[0013] Based on the objective of the present invention of adhering to metal and plastic film, the first requirement of the polyester resin composition is adhesion, and if the product is to be formed, flexibility will also be required, and furthermore, water resistance, weather resistance, chemical resistance, heat resistance, and the like, will be required in order to provide durability to the adhesive layer of the laminated metal plate.

[0014] The polyester resin used in the present invention is a commonly known thermoplastic resin that is the product of condensation between a polybasic acid and a polyhydric alcohol with an arithmetic mean molecular weight between 7000 and 40,000, preferably between 10000 and 30,000.

[0015] Examples of polybasic acids include aliphatic dibasic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, decane-1,10-dicarboxylic acid, and the like; alicyclic polybasic acids such as hexahydrophthalic acid, hexahydrotrimellitic acid, tetrahydrophthalic acid, as well as anhydrides thereof; aromatic polybasic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, as well as anhydrides thereof; and other acids such as maleic acid, fumaric acid, itaconic acid, and the like.

[0016] Examples of polyhydric alcohols include ethylene glycol, propylene glycol, diethylene glycol, 1,2-butylene glycol, 1,6-hexanediol, 1,4-cyclohexane dimethanol, neopentyl glycol, polylactonediol, and the like. Polyester resins are manufactured by condensation polymerization of these acid components and alcohol components in a reaction vessel at a temperature between 200°C and 250°C.

[0017] The oligomer component used in combination with the polyester resin is a polyester oligomer with an arithmetic mean molecular weight between 300 and 5,000, preferably between 1000 and 2000, and has between 0.3 and 5.0 mol/kg, preferably between 1.0 and 3.0 mol/kg of molecules with polymeric unsaturated double bonds.

[0018] The polyester type oligomer can be obtained by ester bonding a (meth)acrylic acid to a low molecular weight polyester with hydroxyl groups having an arithmetic mean molecular weight of 5000 or less, and the low molecular weight polyester can be obtained by condensing a polyhydric alcohol with the aforementioned polybasic acid of the polyester resin composition.

[0019] If the arithmetic mean molecular weight of the aforementioned polyester resin is below 7000, there is a tendency towards poor corrosion resistance and water resistance. On the other hand, if the arithmetic mean molecular weight exceeds 40,000, a high solid content adhesive cannot be obtained.

[0020] Furthermore, if the arithmetic mean molecular weight of the aforementioned oligomer is less than 300, achieving a tack-free adhesive layer before thermal lamination will be difficult. On the other hand if the arithmetic mean molecular weight exceeds 5000, the property of hardening by electron beam will be reduced.

[0021] The formulation amount of oligomer in 100 weight parts of polyester resin is between 2 and 200 weight parts, preferably between 5 and 100 weight parts, and even more preferably between 10 and 50 weight parts. If the formulation amount is less than 2 weight parts, the electron beam-hardening reaction of the adhesive will be insufficient and properties such as retort resistance will be reduced. On the other hand, if the formulation amount exceeds 200 weight parts, achieving a tack-free adhesive layer prior to thermal lamination will be difficult. Furthermore, thermal stability during heat treating of the film-laminated metal plate after electron beam irradiation will deteriorate.

[0022] Examples of the aforementioned stress-relaxing agent which is added to the resin composition consisting of polyester resin and oligomer include silica ($SiO_2 \cdot nH_2O$), bentonite ($Al_2O_3 \cdot 5SiO \cdot 2H_2 O$), clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), talc ($3MgO \cdot 4SiO_2 \cdot 2H_2O$), barium sulfate ($BaSO_4$), and calcium carbonate ($CaCO_3$), and the like.

[0023] If an adhesive containing these stress-relaxing agents is used to manufacture a film-laminated metal plate, the retort resistance of the processing region of the metal plate will be improved. The reason that the retort resistance improves is thought by the present inventors to be because the stress-relaxing agent in the adhesive relieves the stress that occurs during process forming of the metal plate, thus maintaining the stability of the adhesive layer.

[0024] Of the aforementioned stress-relaxing agents, extremely fine silica with a particle size between 0.01 and 0.002 microns has higher stress-relaxing effect and is preferable. The formulation amount of stress-relaxing agent is between 0.5 and 250 PHR (weight parts in the 100 weight parts of resin) preferably between 20 and 100 PHR based on the resin composition consisting of polyester resin and oligomer. If the formulation amount of the stress-relaxing agent is less than 0.5 PHR, there will not be a noticeable increase in the retort resistance in the forming region of the film-laminated metal plate, but on the other hand, if the formulation amount exceeds 250 PHR, the adhesive properties of the adhesive will be reduced.

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[0025] Furthermore, the electron beam-hardening adhesive of the present invention may contain colored pigment (for instance white pigments such as titanium oxide, or a commonly known colored pigment which is used by mixing with said white pigment) if necessary and may be used as both a colored coating and an adhesive. With the present invention, the film-laminated metal plate has an ink layer, and if this ink layer is used as the outer surface of a can, normally a colored layer (normally a white coat) is required beneath a printed ink layer formed by multi-color printing, but if a colored coating adhesive is used, one step can be eliminated from the can manufacturing process, which is extremely advantageous. With the present invention, the electron beam-hardening adhesive is a blend of a resin composition consisting of polyester resin and oligomer with a stress-relaxing agent and if necessary a colored pigment, and is diluted as needed using an organic solvent such as methyl ethyl ketone, or toluene, or the like. Furthermore, the retort resistance of the film-laminated metal plate can be increased by formulating the resin component in the adhesive to have 30% by weight or less of a vinyl resin such as vinyl chloride resin, vinyl acetate resin, vinyl chloride/vinyl acetate copolymer, vinylidene chloride resin, or the like, or a (block) polyisocyanate compound.

[0026] With the present invention, the electron beam-hardening ink is comprising a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyethylene oligomer with an arithmetic mean molecular weight between 300 and 5000 and having between 0.3 to 5.0 mol/kg molecules with polymeric unsaturated double bonds in 100 weight parts of polyester resin.

[0027] The same polyester resin as the polyester resin which is the electron beam-hardening adhesive component may be used as the aforementioned polyester resin. If the arithmetic mean molecular weight of the polyester resin is below 7000, the ink will tend to have poor water resistance, but on the other hand, if the arithmetic mean molecular weight exceeds 40,000, the viscosity will be high and handling will be difficult.

[0028] Furthermore, the same polyester oligomer as the polyester oligomer which is the electron beam-hardening adhesive component may be used as the aforementioned polyester oligomer. If the arithmetic mean molecular weight of the oligomer is less than 300, the ink layer will not easily achieve a tack-free condition and the ink will easily smear, but on the other hand, if the arithmetic mean molecular weight exceeds 5000, electron beam-hardening properties will be reduced.

[0029] If the formulation amount of the polyester oligomer in the electron beam-hardening ink is less than 2 weight parts in 100 weight parts of polyester resin, the hardening reaction by the electron beam will be insufficient and properties such as retort resistance will be reduced, but if the amount exceeds 200 weight parts, the ink layer will not easily achieve a tack-free condition, and the ink will easily smear.

[0030] The colorant used in the electron beam-hardening ink may be any colored pigment or dye normally used to color inks, and either organic or inorganic substances are acceptable. The amount of colorant is not particularly restricted, but normally is within a range between 5 and 300 weight parts in 100 weight parts of total solid content of polyester resin and polyester oligomer.

[0031] If necessary, a stress-relaxing agent which was suggested as a component of the aforementioned electron beam-hardening adhesive may be added to the electron beam-hardening ink. The formulation amount for this stress-relaxing agent is preferably 100 weight parts or less with regards to 100 weight parts of total content of polyester resin and polyester oligomer. Furthermore, the electron beam-hardening ink may be formulated with an organic solvent if necessary, such as methyl ethyl ketone or toluene, or the like.

[0032] Furthermore, in order to increase the retort resistance of the film-laminated metal plate, the resin composition of the electron beam-hardening ink may have 30% by weight or less of a vinyl resin such as vinyl chloride resin, vinyl acetate resin, vinyl chloride resin/vinyl acetate copolymer, vinylidene chloride resin, or the like, and (block) polyisocyanate compound.

[0033] With the present invention, a PET film may be suggested as a representative example of the transparent plastic film which is laminated onto the metal plate using electron beam-hardening adhesive. Between 75 and 100% of the ester repeating units of the PET film consist of ethylene terephthalate units, and ester units such as phthalic acid, isophthalic acid, succinic acid, and adipic acid, and the like, may be suggested as the ester units other than ethylene terephthalate. PET film surface is normally surfaced treated with a Corona discharge treatment, or the like, in order to increase adhesion to the adhesive. Furthermore, with the present invention, a polyethylene film or a polypropylene film, or the like, may be used as the transparent plastic film instead of a PET film.

[0034] With the present invention, examples of the metal plate include hot rolled plate, cold rolled plate, melted zinc or zinc alloy galvanized steel plate, electroplated zinc or zinc alloy galvanized steel plate, tin plate, tin-free steel, chrome-plated sheet steel, aluminum-plated sheet steel, tungsten-plated sheet steel, nickel-plated sheet steel, and other types of alloy-plated sheet steel, stainless steel, aluminum plate, copper plate, titanium plate, and other metal plates, and if necessary these plates may have a chemical treatment such as phosphoric acid treatment, chromate treatment, organic chromate treatment, cobalt complex oxide treatment, nickel substitution plating, and other treatments. Furthermore, metal plate which has a color coating such as a white coat on the surface of the aforementioned metal plates or chemically treated metal plates are included in the metal plate of the present invention. The color coating such as white coat becomes the base layer for printing, and the color coating such as white coat can be used as a base layer for printing on the outside surface of the can.

[0035] Next, an example of a manufacturing method for the film-laminated metal plate will be described. First, electron beam-hardening ink with the desired color is applied at a thickness of between 0.5 and 3 μm using for instance a gravure offset method onto a corona discharge treated PET film with a thickness between 5 and 30 μm, the film is dried to a tack-free condition by heating for several seconds at a temperature between 50°C and 150°C if necessary, a different colored electron beam-hardening ink is similarly applied and dried, in order to perform two color printing on the PET film. Furthermore, a colored coating and electron beam-hardening adhesive into which, for instance, titanium oxide is dispersed, or an electron beam hardened transparent adhesive without colored pigment is applied to a dried film thickness of between 1 and 5 µm using a normal painting means such as a roll coating method, gravure method, gravure offset method, or spray painting, or the like, and then dried, if necessary, for several seconds at a temperature of between 50°C and 150°C until a tack-free condition is achieved. Next, the adhesive layer is overlaid onto a metal plate (for instance, tin plate), and thermally laminated at a temperature below the thermal softening temperature for PET film (less than approximately 230°C) for approximately two seconds or less, in order to obtain a laminated steel plate.

[0036] An electron beam is irradiated through the PET film onto the laminated metal plate obtained thereby in order to harden the film and obtain the objective film-laminated metal plate, and the accelerator of the electron beam-generating source used to a radiate the electron beam may be a Cockcroft accelerator, Cockcroft-Walton accelerator, Van de Graaff accelerator, resonance transformer, transformer, insulated core transformer, Dynamitron, linear fillament, area beam accelerator or high frequency accelerator, or the like. The electron beam energy required to harden the electron beam-hardening adhesive and ink of the present invention is between 100 KeV and 300 KeV, and preferably a range between 150 KeV and 200 KeV is appropriate. A beam intensity of between 0.2 Mrad and 15 Mrad is appropriate, and between 1 Mrad and 5 Mrad is particularly preferable. The irradiation time for the electron beam is normally less than approximately 1 second, which is approximately 1/50th of the time required for thermal hardening.

[0037] The film-laminated metal plate obtained is suitable for use in various types of cans such as cans for beverages, cans for food, 5 gallon cans, and the like. Furthermore, applications such as thermos bottles and refrigerator outside surfaces are also possible.

[0038] PREFFERED EMBODIMENTS

The present invention will be described below using preferred embodiments.

[0039] Manufacturing Polyester Resin

Manufacturing Example 1

18.3 weight parts of dimethyl terephthalate, 11.7 weight parts of dimethyl isoterephthalate, 11.9 weight parts of ethylene glycol, 20.5 weight parts of neopentyl glycol, 118 mg of zinc acetate dihydrate as an ester substitution catalyst, and 246 mg of antimony trioxide as a condensation polymerization catalyst were added to a 1 L autoclave, heated to between 160°C and 210°C, subjected to ester substitution reaction, and the ester substitution reaction was completed two hours later when a stoichiometric amount of methanol had been distilled. Then, a small quantity of trimethyl phosphate was added and mixed for 30 minutes at between 200°C and 210°C. Next, the temperature was increased to 220°C, and 37.6 weight parts of azelaic acid were added and the ester reaction was continued for 30 minutes at a temperature between 220°C and 230°C. Next, the pressure was gradually reduced while the temperature was increased to 250°C, and the excess glycol was removed at 250°C 10 mm Hg. The temperature was further increased and the pressure decreased until obtaining polyester resin (I) with an OH value of 6.5 and an arithmetic mean molecular weight of 30,000. Furthermore, this resin (I) was diluted with a solvent consisting of methyl ketone/cyclohexanone = 50/50 until the heating residue was 30% by weight.

[0040] Manufacturing Example 2

A polyester resin (II) solution was synthesized in accordance with Manufacturing Example 1, using the following composition.

dimethyl terephthalate	22.2 weight parts
dimethyl isophthalate	32.7 weight parts
sebacic acid	19.0 weight parts
ethylene glycol	10.1 weight parts
neopentyl glycol	26.2 weight parts

The arithmetic mean molecular weight of the resin (II) obtained was 25,000.

[0041] Polyester Oligomer Manufacturing Example

Manufacturing Example 3

1.0 moles of trimethylol propane, 2.0 moles of triethylene glycol, 1.0 moles of 1,6-hexanediol, 3.0 mol of adipic acid, and catalytic quantities of dibutyl tin compound were combined, and a polyester with a arithmetic mean molecular weight of approximately 850 and a hydroxyl value of 200 was produced using a commonly known manufacturing method. Next, the polyester obtained was blended with acrylic acid to a ratio of 1.25 equivalents of acrylic acid to 1.0 equivalents of polyester hydroxyl groups, 100 ppm of a polymerization inhibitor (hydroquinone) was added and a reaction proceeded at between 80°C and 100°C, and after the reaction had stopped at a conversion ratio of approximately 85% by weight, the solvent and unreacted acrylic acid were removed by evaporation, and a polyester acrylate oligomer (I) with approximately 3.0 mol/kg molecule of polymeric double bonds was obtained.

[0042] Manufacture of Electron Beam-Hardening Ink (Manufacturing Examples 4 through 7)

Manufacturing Example 4

30 weight parts of red pigment (product name "Red 500 RG," product of Tosoh Corporation) and 20 weight parts of silica (product name "Aerosil 300," product of Japan Aerosil) were added to a resin composition consisting of 10 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 35% by weight solution using methylethyl ketone solvent to make ink R-1.

[0043] Manufacturing Example 5

30 weight parts of blue pigment (product name "Cyanine Blue 5240," product of Dainichiseika Color and Chemicals Mfg. Ltd.) and 20 weight parts of silica (same as Manufacturing Example 4) were added to a resin composition consisting of 30 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (II) solution, and the solid content was adjusted to make a 35% by weight solution using methyl ethyl ketone solvent to make ink B-1.

[0044] Manufacturing Example 6

Ink R-2, a solution with a solid content of 35% by weight, was obtained by the same method as Manufacturing Example 4, except that the formulation amount of polyester acrylate oligomer (I) in Manufacturing Example 4 was changed from 10 weight parts to 20 weight parts, and silica was not added.

[0045] Manufacturing Example 7

Ink B-2, a solution with a solid content of 35%, was obtained by the same method as Manufacturing Example 5, except that the formulation amount of polyester acrylate oligomer (I) in Manufacturing Example 5 was changed from 30 weight parts to 20 weight parts.

[0046] Manufacture of Electron Beam-hardening Adhesive (Manufacturing Examples 8 through 12)

Manufacturing Example 8

80 weight parts of silica (product name "Aerosil 300," product of Japan Aerosil) was added to a resin composition consisting of 20 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive A)

[0047] Manufacturing Example 9

40 weight parts of the silica used in Embodiment 1 was added to a resin composition consisting of 60 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (II) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive B)

[0048] Manufacturing Example 10

100 weight parts of barium sulfate (product name "Bari-fine," product of Sakai Chemical Industry Co. Ltd.), 10 weight parts of vinyl chloride resin (product name "VERR," product of Union Carbide), and 10 weight parts of polyester acrylate oligomer (I) were added to 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive C)

[0049] Manufacturing Example 11

Using the Adhesive A prepared in Manufacturing Example 8, titanium white pigment JR-300 (product of Teikoku Chemical) was dispersed to form a pigment/binder weight ratio = 2 to produce a white coat adhesive. The solid content of the paint was adjusted to 45% by weight. (Adhesive D)

[0050] Manufacturing Example 12

Adhesive E with a solid content of 30% was obtained similar to Manufacturing Example 8, except that the silica of Manufacturing Example 8 was not added.

[0051] Manufacture of Film-laminated Metal Plate

Embodiment 1

The ink R-1 obtained in Manufacturing Example 4 was applied by the gravure offset method to a thickness of approximately 1 μm to make a pattern on the corona discharge treated surface of Ester Film E5100 (12 μm thick PET film) produced by Toyobo Co. Ltd. (corona discharge treated on one side), passed through a drying oven for five seconds at 100°C, and then the ink B-1 obtained in Manufacturing Example 5 was similarly applied and dried. Next, Adhesive A was applied to a thickness of between 2 and 4 μm using gravure application across the entire surface of the PET film with ink layer. The film was then passed through a drying oven for 10 seconds at 100°C to evaporate the solvent component leaving a tack-free condition. This painted PET film and a 0.19 mm thick tin plate Canlite (product of Nippon Steel Corp.) were thermal laminated at a roller pressure force of 5.0 kilograms/cm^2 and a roller temperature of 180°C. Finally, an electron beam was irradiated through the PET film of the laminated metal plate at a current of 50 mA, an intensity of 4 Mrad, and an acceleration voltage of 270 KeV using an electron beam accelerator to harden the adhesive layer and the ink layer in order to obtain a film-laminated metal plate.

[0052] Embodiments 2 ~ 10 and Comparative Examples 1 ~ 3
A film-laminated metal plate was obtained by the same method as Embodiment 1 using the conditions shown in Table 1.

[0053] Welded cans were produced using the film-laminated metal plates obtained by the embodiments and comparative examples with the polyester film as the outer surface of the can body, and then necking was performed to the first stage, second stage, third stage, and fourth stage, and finally bead processing was performed to crimp the lid closed.

[0054] The film-laminated metal plate and can obtained as shown above were subjected to various performance tests, and the results are shown in Table 1. Note, the test methods were as shown below.

[0055] (1) Adhesion 180°C peel: In accordance with JIS K-6744. The peel strength is shown.

[0056] (2) Processability (Dupont impact test): The PET film surface was struck from behind using a 1/2 inch 500 g weight from a height of 50 cm, and the test sample was observed to confirm no peeling between the metal plate and the PET film. Favorable tests where no peeling was observed were evaluated as O.

[0057] (3) Retort resistance: a film-laminated metal plate that had been Erichsen deep draw processed for a beverage can was exposed in tap water steam at an autoclave pressure of 1.4 atm, 125°C x 30 minutes, and then the whitening and adhesive properties were evaluated. The deep drawn conditions were: cutout diameter D60 mm, diameter d33 mm, clearance 0.2 mm, and press force 500 kg/cm^2. Furthermore, a 200 mm diameter welded can formed using the film-laminated metal plate was filled with water and sealed at an autoclave pressure of 1.4 atm, 120°C x 30 minutes and exposed to tap water steam, and the condition of the seam line in the welded area of the can surface and the general surface appearance were visually observed. Favorable tests with no problems were evaluated as O.

[0058] (4) Thermally stable film-laminated metal plate was cut into 5 cm x 5 cm dimensions, heat treated at 200°C for two minutes, and the degree of thermal contraction of the PET film was observed. Tests with no problems or with low thermal shrinkage were evaluated as O.

[0059] Table 1

	Ink type		Adhesive		Electron Beam Irradiation Conditions			Adhesion	Processability	Retort resistance				Thermal stability
	Red	Blue	Type	Thickness (μm)	Voltage KeV	Current mA	Intensity Mrad	180° peel test (g/15 mm)	DuPont impact	Whitening	Adhesion	Seam line condition	Appearance	
Embodiment 1	R-1	B-1	A	3	270	50	4	500	O	O	O	O	O	O
Embodiment 2	R-2	B-2	A	3	250	40	5	550	O	O	O	O	O	O
Embodiment 3	R-1	B-2	A	2	250	40	3	600	O	O	O	O	O	O
Embodiment 4	R-2	B-1	A	4	270	50	4	500	O	O	O	O	O	O
Embodiment 5	R-2	B-1	B	3	270	50	4	450	O	O	O	O	O	O
Embodiment 6	R-1	B-2	B	2	250	40	3	500	O	O	O	O	O	O
Embodiment 7	R-1	B-1	C	3	270	50	4	500	O	O	O	O	O	O
Embodiment 8	R-2	B-2	C	4	270	50	5	600	O	O	O	O	O	O
Embodiment 9	R-2	B-1	D	3	270	50	4	500	O	O	O	O	O	O
Embodiment 10	R-1	B-2	D	2	250	40	3	450	O	O	O	O	O	O
Comparative Example 1	R-162*1	R-39*2	A	3	270	50	4	400	O	Slight whitening of the processing area	30% pealing in the processing area	O	O	O
Comparative Example 2	R-162*1	R-39*2	B	3	270	50	4	400	O	Slight whitening of the processing area	30% pealing in the processing area	O	O	O
Comparative Example 3	R-1	B-1	E	3	270	50	4	350	O	O	30% pealing in the processing area	O	O	O

[0060] The (Notes) in Table 1 are as shown below.

*1 R162: standard laminating ink, product name "Lamistar R162 Red," color red, produced by Toyo Ink Manufacturing.

*2 R39: standard laminating ink, product name "Lamistar R39 Indigo," color blue, produced by Toyo Ink Manufacturing.

[0061] EFFECT OF THE INVENTION

The film-laminated metal plate obtained by the present invention has excellent adhesion between the plastic film, ink, and metal plate, and has excellent retort resistance and particularly retort resistance in the forming region when used as a can for foods. Furthermore, if a plastic film with an ink layer is laminated onto a metal plate using the polyester resin electron beam-hardening adhesive of the present invention, there are advantages in that the process can be performed at high speed and low temperature, and because electron beam hardening is possible, the hardening time for the ink and the adhesive can be dramatically shortened, and as a result plant space can be greatly conserved. Moreover, with the present invention, hardening of the ink and the adhesive does not require that the electron beam irradiation environment be a perfect nitrogen environment, so there is the advantage that the electron beam hardening can be performed in air.